

University of Groningen

Cyclopentadienylvanadium(III) and -vanadium(II) Methyl, Phenyl, and Borohydride Compounds

Hessen, Bart; Teuben, Jan H.; Lemmen, Timothy H.; Huffman, John C.; Caulton, Kenneth G.

Published in:
Organometallics

DOI:
[10.1021/om00124a030](https://doi.org/10.1021/om00124a030)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1985

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Hessen, B., Teuben, J. H., Lemmen, T. H., Huffman, J. C., & Caulton, K. G. (1985).
Cyclopentadienylvanadium(III) and -vanadium(II) Methyl, Phenyl, and Borohydride Compounds.
Organometallics, 4(5). <https://doi.org/10.1021/om00124a030>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

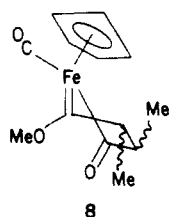
The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

6 would be favored over 8. Consistent with this prediction was an observed NOE effect between Cp and OCH₃ and the absence of such an effect between Cp and either methyl.^{23,24}



The facility of the rearrangement of 2 to 6 is striking and probably results from a combination of methoxy acceleration and relief of strain. Thus, the methoxy must favor this reaction since its position on saturated carbon can do little to stabilize 2 while conjugation with the p orbital in the carbene should have a significant impact on the energy of 4. It is more difficult to assess the contribution of strain relief to this reaction because even though there would be little question that ring strain on the cyclopropane side of the equilibrium is about 25 kcal/mol,²⁵ the strain on the metallacyclobutene side is not known. Were the rearrangement to a carbocycle, strain would slightly favor the cyclopropane; however, small ring metallocycles are probably much less strained than their carbocyclic analogues.²⁶ However, it is unlikely that relief of ring strain, alone, is sufficient to induce the rearrangement since photolysis of cyclopropyl σ -complexes with α -hydrogens showed no reaction.²⁷

Attempts to obtain evidence for the intermediacy of 3 in the rearrangement sequence by studying the effect of added CO on the rate of rearrangement were inconclusive due to the photoinduced decomposition of 6 which was retarded by the presence of CO. However, the mechanism in Scheme I is probably correct in view of the known photobehavior of Fp-alkyl complexes²⁸ as well as our successful isolation of the primary rearrangement product (corresponding to 4) from rearrangement of cyclobutyl²⁹ and cyclobutenyl³⁰ complexes. These results as well as anticipated mechanisms studies on the rearrangement of 2 to 6 will be provided in future papers.

Acknowledgment. This work was partially supported by the National Science Foundation to whom we are grateful. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. High-field NMR spectra were obtained on a Nicolet NT-300 spectrometer, operating at a field of 7 T; therefore acknowledgment is made to the Instrument Program, Chemistry Division, National Science Foundation, for financial assistance in the purchase of the instrument. We are also grateful to W. R. Winchester for providing the aforementioned EHMO calculations.

Cyclopentadienylvanadium(III) and -vanadium(II) Methyl, Phenyl, and Borohydride Compounds

Bart Hessen and Jan H. Teuben*

Department of Inorganic Chemistry, University of Groningen
9747 AG Groningen, The Netherlands

Timothy H. Lemmen, John C. Huffman, and
Kenneth G. Caulton*

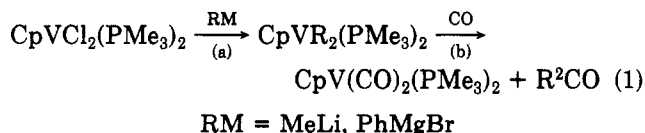
Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

Received December 10, 1984

Summary: Reaction of CpVCl₂(PMe₃)₂ with MeLi and PhMgBr yields CpVMe₂(PMe₃)₂ and CpVPh₂(PMe₃)₂, respectively. Conproportionation of CpVCl₂(PMe₃)₂ and CpVMe₂(PMe₃)₂ gives selective conversion to CpVMe(CI)(PMe₃)₂. These paramagnetic compounds show isotropic ¹H NMR shifts of the P-Me protons. CpVMe₂(PMe₃)₂ reacts rapidly with CO to give acetone and *diag*-CpV(CO)₂(PMe₃)₂. Borohydride converts CpVCl(Me₂PCH₂CH₂PMe₂) to CpV(η^2 -BH₄)(dmpe), shown to have one unpaired electron, two less than its chloride precursor. Conversion of this monochloride to CpVR(dmpe) occurs with MeLi and PhMgBr. The monomethyl compound has a low VC-H stretching frequency (2750 cm⁻¹), but the crystal structure shows no agostic hydrogen to be involved. Crystal data (-158 °C): *a* = 12.526 (3) Å, *b* = 9.285 (2) Å, *c* = 12.772 (3) Å, *Z* = 4 in space group *P*2₁2₁2₁.

Complexes of the early transition metals containing one η^5 -C₅H₅ ligand are currently under study¹⁻⁶ since they are less sterically encumbered and offer more metal orbitals for transformations of coordinated ligands than do their bis(η^5 -C₅H₅) relatives. Among early transition metals, representatives of the first transition series are particularly interesting since they offer a situation atypical in organometallic chemistry, that of isolable paramagnetic compounds. For example, all monomeric CpV²⁺ compounds, although d², contain two unpaired electrons.^{7,8} We report here the synthesis of methyl and phenyl compounds of the CpV²⁺ and CpV⁺ fragments, as well as their characterization by selected physical methods and reactivity studies.

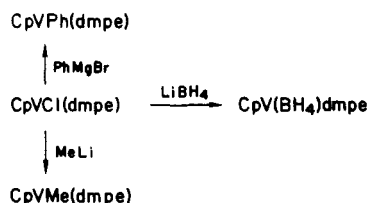
As summarized in eq 1a, purple-blue CpVCl₂(PMe₃)₂ can be converted, in Et₂O at -30 °C, to red CpVR₂(PMe₃)₂, R = Me and Ph.⁹ Both air-sensitive compounds can be



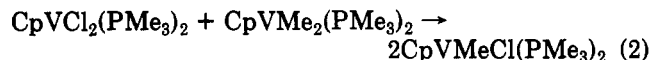
- (21) Hoffmann, R.; Lipscomb, W. N. *Chem. Phys.* **1962**, *36*, 2176.
- (22) Hoffmann, R.; Thibault, J. C.; Burgi, H. B.; Ammeter, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
- (23) Sanders, J. K. M.; Hall, L. D. *J. Am. Chem. Soc.* **1980**, *102*, 5703.
- (24) Sanders, J. K. M.; Marsh, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 353.
- (25) Benson, S. W., Ed. "Thermochemical Kinetics"; Wiley: 1968; p 179.
- (26) Cosimo, R. D.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 948.
- (27) Manganiello, F. J.; Christensen, L. W.; Jones, W. M. *J. Organomet. Chem.* **1982**, *235*, 327.
- (28) Cf. Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766.
- (29) Unpublished results of Y. Stenstrom, University of Florida.
- (30) Unpublished results of G. Klauk, University of Florida.

- (1) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295.
- (2) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793 and references therein.
- (3) Blenkins, J.; de Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483 and references therein.
- (4) Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem.* **1984**, *96*, 445 and references therein.
- (5) Wells, N. J.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1981**, *213*, C17.
- (6) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157.
- (7) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.
- (8) Nieman, J. Thesis, University of Groningen, Groningen, The Netherlands, 1983.

Scheme I



manipulated in hydrocarbon solvents under N_2 at 25 °C. Both compounds are paramagnetic, and the isotropic shifts of the resonances of the phosphine methyl hydrogens serve as useful spectroscopic probes. For example, it is possible to use ^1H NMR to demonstrate that the reaction in eq 2



occurs (<12 h) at 25 °C in Et_2O not statistically, but essentially to completion. The mixed methyl chloro complex¹⁰ isolated from eq 2 is also paramagnetic and is not accessible from the 1:1 reaction of $\text{CpVCl}_2(\text{PMe}_3)_2$ with MeLi at -20 °C (followed by prompt workup); instead at 50% yield of $\text{CpVMe}_2(\text{PMe}_3)_2$ results. A thermodynamic bias for dispersing π -donor ligands (e.g., Cl, OR) has been observed before for Ti(IV) complexes.¹¹ Equation 2 is not rapid on the isotropically shifted ^1H NMR time scale, nor have we observed rapid exchange of $\text{CpVMe}_2(\text{PMe}_3)_2$ with free PMe_3 .

Both the dimethyl and the diphenyl compounds react rapidly (eq 1b) with 1 atm CO to eliminate the corresponding ketones and produce the same V(I) carbonyl $\text{CpV(CO)}_2(\text{PMe}_3)_2$,¹² isolated as the *diagonal* isomer.

An attempt to form a borohydride derivative of $\text{CpVCl}_2(\text{PMe}_3)_2$ using 1 mol of LiBH_4 yielded $\text{CpVCl}(\text{PMe}_3)_2$ (i.e., V(II)). Consequently, efforts were concentrated on direct preparation of a V(II) borohydride complex (Scheme I). CpVCl(dmpe) ,⁷ with three unpaired electrons,⁸ is readily converted into $\text{CpV(BH}_4\text{)dmpe}$,¹³ whose ^1H NMR appears to show only one dmpe CH_2 chemical shift (13 ppm, fwhm 256 Hz),¹⁴ and a dmpe methyl chemical shift (-12.9 ppm, fwhm 600 Hz) with a shoulder on the downfield side. The infrared spectrum (Nujol, KBr) is equally problematic, exhibiting a pattern (2380 (s), 2345 (s), 2255 (s), 1855 (m, br) cm^{-1}) not clearly conforming to the proposed guidelines¹⁵ for η^1 -, η^2 -, or $\eta^3\text{-BH}_4$ -binding. The preliminary results of a single-crystal diffraction study on a twinned crystal show $\eta^5\text{-C}_5\text{H}_5$, $\eta^2\text{-BH}_4$ and $\eta^2\text{-dmpe}$ coordination. If we count $\eta^5\text{-Cp}$ as utilizing three orbitals on vanadium and $\eta^2\text{-BH}_4$ as requiring n orbitals on vanadium, it is predicted that the seven orbitals required to bind $\eta^5\text{-Cp}$, $\eta^2\text{-dmpe}$, and $\eta^2\text{-BH}_4$ will force spin pairing among the three d electrons in $\text{CpV(BH}_4\text{)dmpe}$.

(9) For red $\text{CpVMe}_2(\text{PMe}_3)_2$, crystallized from pentane (C and H elemental analysis): ^1H NMR (360 MHz, C_6D_6 , 20 °C, shifts relative to Me_4Si (δ 0), downfield shifts positive) PMe at -3.9 (940) ppm. The compound is paramagnetic with $\mu_{\text{eff}} = 2.74 \mu_{\text{B}}$ (solid sample, 80-300 K, Faraday method). For brown-red $\text{CpVPh}_2(\text{PMe}_3)_2$, crystallized from Et_2O (C, H, and V elemental analysis): ^1H NMR (360 MHz, C_6D_6 , 20 °C) PMe at -10.8 (1200) ppm. Full-width at half maximum, in Hz, is given in parentheses after the chemical shift.

(10) For dark brown $\text{CpVMeCl}(\text{PMe}_3)_2$, crystallized from Et_2O : $\nu_{\text{VC-H}}$ 2805 cm^{-1} ; ^1H NMR (360 MHz, C_6D_6 , 21 °C) PMe at -9.5 (1620).

(11) Marsella, J.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* 1980, 201, 89.

(12) Rehder, D. *J. Magn. Reson.* 1977, 25, 177.

(13) The EI mass spectrum shows a parent ion.

(14) For comparison, the 360-MHz ^1H NMR of CpVCl(dmpe) at 25 °C shows Cp at 243 (6000) ppm, methyl resonances at 2.4 (460) and -25.5 (520) ppm, and methylene resonances at 16.8 (560) and 8.9 (720) ppm.

(15) Marks, T. J.; Kolb, J. R. *Chem. Rev.* 1977, 77, 263.

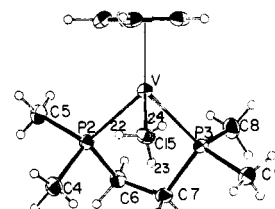


Figure 1. ORTEP drawing of $(\eta^5\text{-C}_5\text{H}_5)\text{VCH}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$. Hydrogens on methyl group bound to vanadium are indicated by small numbers only. Selected structural parameters: $\text{V-P}(2) = 2.4626$ (12) Å, $\text{V-P}(3) = 2.4709$ (12) Å, $\text{V-C}(15) = 2.219$ (4) Å; $\angle\text{P}(2)\text{-V-P}(3) = 81.11$ (4)°, $\angle\text{P}(2)\text{-V-C}(15) = 92.67$ (12)°, $\angle\text{P}(3)\text{-V-C}(15) = 90.83$ (12)°.

This agrees with the measured solution magnetic moment,¹⁶ $1.6 \mu_{\text{B}}$ at 25 °C, while the "high-spin" compound CpVMe(dmpe) has the expected moment of $3.6 \mu_{\text{B}}$. This "orbital counting" formalism also correctly explains the one unpaired electron observed for $\text{CoH}(\eta^2\text{-BH}_4)(\text{PCy}_3)_2$ ¹⁷ and predicts diamagnetism for $\text{Cp}_2\text{V}(\eta^2\text{-BH}_4)$ (magnetic susceptibility not reported).¹⁸

Preparation of two cyclopentadienylvanadium(II) hydrocarbyls proceeds as in Scheme I. Each compound¹⁹ exhibits isotropically shifted dmpe proton signals indicative of two methyl and two methylene environments. Particularly puzzling is the observation that the methyl group bound to vanadium in CpVMe(dmpe) exhibits a C-H stretching frequency of 2750 cm^{-1} , which is lower than that in $\text{CpVMe}_2(\text{PMe}_3)_2$ (2795 cm^{-1}), Cp_2TiMe_2 ,²⁰ BMe_3 ,²¹ Al_2Me_6 ,²² or any of the high-valent metal/methyl complexes synthesized by the Wilkinson group.²³ With little prospect of settling this problem by ^{13}C or ^1H NMR studies of paramagnetic CpVMe(dmpe) , we have determined its crystal structure²⁴ (Figure 1). The molecule is a monomeric three-legged piano stool, and the V-CH₃ unit shows no evidence of an agostic²⁵ hydrogen; the V-C-H angles are 105 (4)°, 122 (3)°, and 105 (5)°, with internal H-C-H angles being 105 (5)°, 117 (6)°, and 104 (6)°. Since this is the first V(II) methyl compound synthesized and structurally characterized, evaluation of the significance of the V-C distance (2.219 (4) Å) is difficult. This distance is considerably longer than V-C found in V(III) complexes such as $\text{Cp}_2\text{V(C}\equiv\text{C-}t\text{-Bu)}$, 2.075 (5) Å,²⁶ or $\text{V}(\text{C}_6\text{Me}_3\text{H}_2)_3\cdot\text{THF}$, 2.116 (7)/2.099 (6)/2.113 (7) Å²⁷ but similar to those in the vanadocene adduct $\text{Cp}_2\text{V}(\text{EtO}_2\text{CCH=CHCO}_2\text{Et})$, 2.186/2.213 (12) Å.²⁸ Also, com-

(16) Evans, D. F. *J. Chem. Soc.* 1959, 2003.

(17) Nakajima, M.; Moriyama, H.; Kobayashi, A.; Saito, T.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* 1975, 80.

(18) Marks, T. J.; Kennelly, W. J. *J. Am. Chem. Soc.* 1975, 97, 1439.

(19) For black CpVMe(dmpe) , crystallized from Et_2O /pentane (C, H, V elemental analysis): ^1H NMR (200 MHz, C_6D_6) Cp at +243 (4000) ppm, PMe at +19 (440) and -14 (400) ppm, and CH₂ at +34 and +31.8 ppm. For black CpVPh(dmpe) : ^1H NMR (360 MHz, C_6D_6 , 21 °C) PMe at -11.25 (630) and +9.1 (570) ppm and CH₂ at +33 (570) with a shoulder at +35 ppm.

(20) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* 1956, 3, 104.

(21) Woodward, L. A.; Hall, J. R.; Dixon, R. N.; Sheppard, N. *Spectrochim. Acta* 1959, 15, 249.

(22) Gray, A. P. *Can. J. Chem.* 1963, 41, 1511.

(23) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1976, 1488 and references therein.

(24) Crystals grown from Et_2O /pentane assume space group $P2_12_12_1$ with (-158 °C) $a = 12.526$ (3) Å, $b = 9.285$ (2) Å, $c = 12.772$ (3) Å, and $Z = 4$. $R(F) = 3.2\%$ for 1797 reflections. All hydrogens were refined isotropically. A complete tabulation of crystallographic parameters and bond lengths and angles is available as supplementary material.

(25) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395.

(26) Evans, W. J.; Bloom, F.; Doedens, R. J. *J. Organomet. Chem.* 1984, 265, 249.

(27) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1984, 886.

parison to the Ti-C₂H₅ distance involving the inherently larger Ti(O) in (η^7 -C₇H₇)Ti(C₂H₅)(dmpe), 2.211 (5) Å,²⁹ permits the conclusion that CpVMe(dmpe) contains a somewhat long V-CH₃ bond.

The distinctly low V-Me C-H stretching frequency in CpVMe(dmpe) thus finds no explanation in the X-ray study. We suggest that one of the half-filled orbitals is not only metal localized but also V-C and C-H antibonding. This would account for the IR anomaly, the lack of observation of the V-CH₃ proton resonance, and also the long V-C distance.

Acknowledgment. This work was supported by the U.S. National Science Foundation (Grant CHE-8305281) and by NATO (NATO Research Grant No. 070-82).

Supplementary Material Available: Tables of atomic positional parameters and bond lengths and angles for (C₅H₅)-VCH₃(Me₂PCH₂CH₂PM₂), a listing of *F*_o and *F*_c for CpVMe(dmpe), and tables of elemental analyses and magnetic susceptibility data (18 pages). Ordering information is given on any current masthead page.

(28) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, A. *Inorg. Chem.* 1979, 18, 2281.

(29) Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. J. *Chem. Soc., Chem. Commun.* 1983, 356.

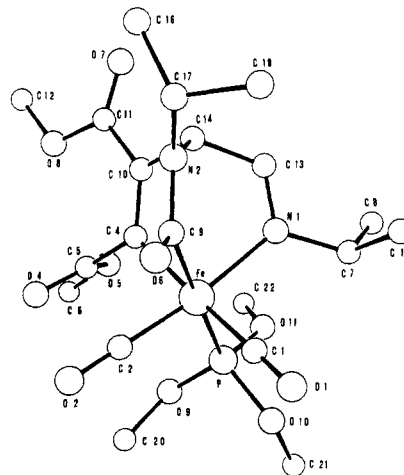
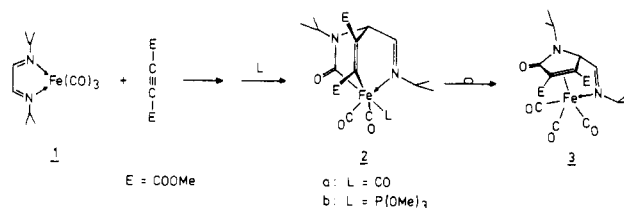


Figure 1. The molecular structure of 2b. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe-C(4) = 2.023 (3), Fe-C(9) = 2.023 (3), Fe-N(1) = 2.030 (2), Fe-C(1) = 1.808 (3), Fe-C(2) = 1.767 (3), Fe-P = 2.260 (1), C(4)-C(10) = 1.337 (4), C(9)-N(2) = 1.362 (4), N(1)-C(13) = 1.269 (4), C(9)-Fe-P = 178.8 (1), C(1)-Fe-C(4) = 173.7 (1), C(2)-Fe-N(1) = 170.8 (1), C(4)-Fe-C(9) = 87.6 (1).

Scheme I



1,5-Dihydropyrrol-2-ones from (1,4-Diaza-1,3-diene)tricarbyliron and Alkyne. 2.¹ Structure of a [2.2.2] Bicyclic Intermediate with Iron at the Bridgehead Position

Hans-Werner Frühauf,^{2a,b} Frank Seils,^{2a}
Richard J. Goddard,^{2c} and Maria J. Romão^{2c,d}

FB 6, Organische Chemie der Universität-Gesamthochschule
Duisburg 1, West Germany
Max-Planck-Institut für Strahlenchemie and
Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim, West Germany

Received December 18, 1984

Summary: (1,4-Diaza-1,3-diene)tricarbyliron complexes react with electron-deficient alkynes under an atmosphere of CO to give a thermally labile, bicyclic intermediate which rearranges to a (1,5-dihydropyrrol-2-one)tricarbyliron complex. With trimethyl phosphite instead of CO, the intermediate is stabilized, and it has been possible to determine its structure by X-ray crystallography.

Until recently it was thought that C-C bond-forming reactions of 1,4-diaza-1,3-dienes (dad) in the coordination sphere of transition metals were only feasible in binuclear complexes with the dad coordinated to both metal centers in an unsymmetrical six-electron mode, involving the π -electrons of one C=N moiety.^{3,4} The reaction of (dad)-

tricarbyliron complexes 1, in which the dad is coordinated in the chelating 4-electron mode through the nitrogen lone pairs only, with dimethyl acetylenedicarboxylate under an atmosphere of CO, finally yielding tricarbyliron complexes of 1,5-dihydropyrrol-2-ones (e.g., 3, see Scheme I) suggests that this is not the case.¹ This is supported by the observation of a thermally labile mononuclear intermediate 2a. In view of the importance of this reaction,⁵ we decided to investigate the structure of 2a. The ¹³C NMR resonances of this intermediate could be fully assigned from the proton-coupled spectra and revealed shift differences of up to 125.5 ppm with respect to the isomerized product 3 (cf. Figure 2), consistent with a [2.2.2] bicyclic structure. Unfortunately, the structure of this intermediate could not be determined by X-ray methods. However, when the reaction was performed in the presence of trimethyl phosphite,⁶ a compound with very similar spectroscopic properties to 2a was isolated.⁷

(3) Frühauf, H.-W.; Landers, A.; Goddard, R.; Krüger, C. *Angew. Chem.* 1978, 90, 56; *Angew. Chem., Int. Ed. Engl.* 1978, 17, 64.

(4) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* 1982, 21, 151.

(5) Not only are the 1,4-diaza-1,3-dienes easily accessible starting materials, but the pyrrolinones formed are of considerable synthetic interest. See: (a) Kocher, K. S.; Carson, H. J.; Clouser, K. A.; Elling, J. W.; Grames, L. A.; Parry, J. L.; Sherman, H. L.; Braat, K.; Pinnik, H. W. *Tetrahedron Lett.* 1984, 25, 1871. (b) Rio, G.; Masure, D. *Bull. Soc. Chim. Fr.* 1972, 4598 and references cited therein.

(6) Preparation of 2b: A solution of 0.67 g (2.4 mmol) of (glyoxalbis(isopropylimine))tricarbyliron 1¹² in ca. 20 mL of tetrahydrofuran (THF) was cooled to -15 °C. Then 0.283 mL (298 mg, 2.4 mmol) of trimethyl phosphite (z. Synth.; E. Merck, Darmstadt) was added, followed slowly from a dropping funnel by a solution of 341 mg (2.4 mmol) of dimethyl acetylenedicarboxylate in 30 mL of THF, keeping the reaction temperature below -5 °C. After removal of the solvent in vacuo, the vesicular residue was redissolved in 25 mL of methanol at 0 °C. After the mixture was slowly cooled to -78 °C, 0.65 g of a light yellow crystalline powder was precipitated. It was dried in vacuo. The concentrated mother liquor yielded an additional 0.11 g; total yield 0.76 g (58%).

(1) Part 1: Frühauf, H.-W.; Seils, F.; Romão, M. J.; Goddard, R. J. *Angew. Chem.* 1983, 95, 1014; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 992; *Angew. Chem. Suppl.* 1983, 1435.

(2) (a) Universität Duisburg. (b) Max-Planck-Institut für Strahlenchemie. (c) Max-Planck-Institut für Kohlenforschung. (d) Present address: Department of Chemistry, Lisbon University, Lisbon, Portugal.